SrAl$_2$O$_4$ spinel phase as active phase of transesterification of rapeseed oil

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ABSTRACT

The transesterification of rapeseed oil and methanol was investigated over binary oxide (SrO)(Al$_2$O$_3$) catalyst. Effect of the reaction conditions such as: methanol to oil molar ratio, reaction temperature, reaction time and catalyst loading level was extensively studied in this work. The most optimal process parameters have been reported. The physicochemical characteristics of binary oxide were analyzed by FTIR spectroscopy, X-ray diffraction (XRD), BET, SEM-EDS methods. The highest triglycerides (TG) conversion and methyl ester yields was obtained for (SrO)(Al$_2$O$_3$) calcined at 600 °C after two hours conducting at 160 °C (molar ratio Oil: methanol = 1: 6, catalyst weight m = 1.95 g) and were equal 90.5 and 89%, respectively. It was proven that the SrAl$_2$O$_4$ spinel structure is the active phase taking part in the process of conversion of TGs to biodiesel.

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1. Introduction

Intensive increase in fuel prices, as well as contraction of the oil and coal resources, have increased interest in alternative energy sources, which is directly related to the development of new technologies for biodiesel production which in the long run could play an important role in the near future [1]. Biodiesel is a promising nontoxic and biodegradable renewable fuel comprised of mono-alkyl esters of long chain fatty acids. This fuel is free of sulphur and it is cleaner burning fuel than petroleum diesel with reduced emissions of SO$_x$, CO, unburnt hydrocarbons and particulate matter [2].

One of the most known method of biodiesel production in the literature data is transesterification of rapeseed oil. Transesterification is the most effective, economically viable and most common process used in industrial scale. However, there is still a need to develop and optimize the reaction conditions as well as the selection of the most active and selective catalyst for the production of biodiesel [3]. The best known materials used in the transesterification reaction are heterogeneous and homogeneous catalysts [4–7].

Typical alkaline heterogeneous catalysts which are used in the production of biodiesel include the following systems: CaO,

CaTiO$_3$, CaZrO$_3$, CaO, CeO$_2$, CaMnO$_3$, Ca$_2$Fe$_2$O$_5$, KOH/Al$_2$O$_3$, KOH/NaY, Al$_2$O$_3$/Kl, ETS-10 zeolite, alumina/silica supported K$_2$CO$_3$. Whereas, acidic catalysts include the following systems: ZnO/I$_2$, ZrO$_2$/SO$_4$, TiO$_2$/SO$_4$, carbon-based solid acid catalyst, vanadyl phosphate, niobic acid, sulfated zirconia, Amberlyst-15, Nafion-NR50. The main factor in favour of using heterogeneous catalysts in the studied reaction is the ease of separating the catalyst from the reaction product and able to be recycled. The disadvantage of all heterogeneous catalysts is the fact that a small portion of the catalyst goes into solution thus affecting on the catalytic activity in the studied reaction. Based on the reasons mentioned above we decided to prepare the heterogeneous systems containing the spinel type structure which will limit the passage of the catalyst into the reaction solution [6,7].

Generally SrAl$_2$O$_4$ system is obtained as a result of the high temperature annealing without a flux usually it is temperature of 1400–1600 °C. In addition to annealing method a lot of chemical methods are well known for the synthesis of this material. The most well known methods include: the combustion synthesis of SrAl$_2$O$_4$, a sol–gel method [8,9], a spray-drying aqueous solutions of strontium and aluminium nitrates [10], a precipitate [11], a solid-state reaction [12], a hydrothermal reaction [13], a sputtering method [14].

Therefore, the main goal of this work is to explain the influence of SrAl$_2$O$_4$ spinel system on activity results in transesterification of rapeseed oil. In order to achieve the intended purpose of this work binary oxides (SrO)(Al$_2$O$_3$) were synthesized by

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co-precipitation method and used as the active catalyst material in transesterification reaction of rapeseed oil. Furthermore, the crystallization behaviour, sorption properties of catalysts in relation to methanol as one of the reaction reagents and basicity of prepared systems was also studied in this work. The concentration of the strontium ions in the reaction product solution was monitored in order to examine the impact of these ions on the investigated process.

2. Experimental part

2.1. Samples preparation

In order to prepare $(SrO)(Al_2O_3)$ binary oxides the following molar ratio of Sr: Al = 0.5 strontium nitrate and aluminium nitrate compounds were used. Aqueous solutions of 1 M/L strontium nitrate and 1 M/L aluminium nitrate were mixed in appropriate quantity under vigorous stirring at 80 °C. A concentrated ammonia solution was then added by dropwise addition until the pH reached values of between 10 and 11 and then the mixtures were stirred for another 30 min. The resulting fine precipitates were washed two times in deionised water and then dried at 120 °C for 15 h and calcined for 4 h at 600, 900 and 1200 °C in air for 4 h.

2.2. Methods of samples characterization

The specific surface area and porosity of catalysts and their supports were determined with automatic sorptometer Micromeritics ASAP 2020 V3.05 G (Surface Area and Porosity Analyzer). Samples were prepared at 350 °C during 2 h evacuation and after that low temperature nitrogen adsorption–desorption measurements were carried out using BET, liquid N_2 method.

Powder X-ray diffractograms were recorded on a PAN analytical X'Pert Pro MPD using Cu K$_\alpha$ radiation (λ = 154.05 pm) in 2θ range of 5–90°.

The TPD-CO_2 measurements were carried out in a quartz reactor using CO_2 as probe molecule. The CO_2 was adsorbed in the $SrAl_2O_4$ catalysts at 50 °C for 30 min after drying in flowing He at 600 or 800 °C for 60 min. Samples were calcined at 600, 900 or 1200 °C for 4 h in static air before each TPD-CO_2 experiment. The temperature programmed desorption of CO_2 was carried out in the temperature range 100–600 °C, after removing physisorbed CO_2 from the catalyst surface.

The SEM measurements were performed using a S-4700 scanning electron microscope HITACHI (Japan), equipped with an energy dispersive spectrometer EDS (Thermo Noran, USA). Images were recorded at several magnifications using secondary electron or BSE detector. The EDS method made it possible to determine the qualitative analysis of elements present in the studied micro-area of sample surface layer on the basis of the obtained characteristic X-ray spectra. A map of the distribution of elements on the studied micro-area was made. The accelerating voltage was 25 kV. For performing, measurements samples were coated with carbon target using Cressington 208 HR system.

Infrared spectra were recorded with a IRTracer-100 FTIR (Shimadzu) spectrometer equipped with a liquid nitrogen cooled MCT detector. Before analysis the sample was heated at 400 °C in an argon stream (50 cm^3/min). A resolution of 4.0 cm^{-1} was used throughout the investigation. 64 scans were taken to achieve a satisfactory signal to noise ratio. The background spectrum was collected at 50 °C after the process of heating. Then the argon mixture was shifted to a mixture of approximately 1 vol.% CH_3OH in argon stream. The adsorption process involved exposure of the heated catalysts to 1 vol.% CH_3OH in argon stream flowing at 50 cm^3/min

Table 1
Optimized gradient of phase used to LC analysis.

Solvent A: methanol
Solvent B: 2-propanol/hexane = 4/5
Injection Volume: 2 μL
Column Temperature: 30 °C

Mobile phase gradient			Flow rate ml·min^{-1}
Time (min)	Solvent A (%)	Solvent B (%)	
0.0	100	0	0.25
20.0	100	0	0.25
45.0	0	100	1
55.0	0	100	1
55.0	100	0	1
60.0	100	0	1

for 30 min under atmospheric pressure. After the adsorption process, the cell was evacuated for 15 min at the same temperature in argon.

2.3. Catalytic tests

Prior to analysis of the reaction products, the rapeseed oil composition was analyzed by GC–MS technique. Before GS–MS analysis the oil has undergone a process of derivatization to fatty methyl esters according to the international standard ISO 12966-2:2011. Quantitative studies were carried out over HAWLETT PACKARD 5890 SERIES II Gas Chromatograph equipment. Zebron ZB-1MS capillary column (30 m length, 0.25 mm thickness and 0.25 mm diameter) was used for the analysis of rapeseed oil composition. Ultra pure helium gas was used as a carrier gas, temperature gradient was set from 70 to 250 °C in the course of 55 min with a ramp rate 8 °C/min and then kept at 250° for 30 min. The applied method showed good resolution between palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), bohenic (C22:0), erucic (C22:1) fatty acid methyl esters. Quantitative analysis of fatty acid methyl esters were done using an internal standard method. The amounts of individual components were calculated based on the formula shown below.

$$M_x = \frac{S_x}{S_{wz}} \times \frac{M_{wz}}{f}$$

where M_x – mass of the fatty methyl ester, M_{wz} – mass of the internal standard, S_x – area of the fatty methyl ester, S_{wz} – area of the internal standard, f – response factor.

For determination of each fatty methyl esters the response factor was used according to the work [15].

The transesterification process were carried out in an autoclave using a substrate mixture of rapeseed oil and CH_3OH with molar ratio 6/1; 9/1 and 12/1 and catalysts weight of 0.975 and 1.95 g. Reaction was performed in temperature range 100–160 °C for 1–4 h under pressure 50 Barr. Before reaction tests, catalysts were calcined at 600, 900 and 1200 °C for 4 h.

The reaction products were analyzed by LC–MS coupled technique (Agilent 1100). Analytical method using in this work for the study of the transesterification reaction products was previously applied by Kondamudi et al. [16]. Liquid chromatograph was equipped with column C-18 and as eluent was used mixture of 2-isopropanol-hexane (4/5) and methanol. The mobile phase gradient was shown in Table 1. For analysis of post-reaction mixture, two detectors were used – DAD (wavelength: λ = 205 nm) to define of triglycerides conversion and mass detector to identification of transesterification process products. The ionization of analyzed mixture were carried out by using Electrospray technique (3000 V, positive ionization; nitrogen flow: 8 L/min^{-1}, nebulizer pressure: 30 psig; gas temperature: 300 °C) [16].

Table 2
Results of BET surface area, monolayer capacity and average pore radius.

Catalyst material	Temperature calcination (°C)	BET surface area (m²/g)	Monolayer capacity (cm³/g)	Average pore radius (nm)
Al_2O_3	400	237	54.5	2.5
$SrAl_2O_4$	600	89	20.4	3.1
$SrAl_2O_4$	900	77	17.6	4.9
$SrAl_2O_4$	1200	2	–	–

The analytic procedure:

1. Post-reaction mixture was centrifuged by using laboratory centrifuge MPW-2 (2000 turnover/min, 30 min) in the aim of removal of catalyst,
2. The rest of catalyst microparticles in product were removed by vacuum filtration,
3. The obtained liquid products were diluted with n-hexane (a hundredfold dilution),
4. Such prepared solution of reaction products were put in analytic vial and loaded on HPLC by using autosampler.

TG conversion was calculated according to the following equation base on HPLC analysis.

$$\text{Conv.} \quad (\%) = \frac{TG_{in} - TG_{out}}{TG_{in}} \times 100\%$$

where, TG_{in} – the total area under the peaks assigned to the TG in rapeseed oil, TG_{out} – the sum of the areas of TG peaks in the product.

The FAME (Fatty acid methyl ester) yield was calculated as the sum of the areas of all FAME peaks relative to the sample containing the methyl esters.

### 2.4. Analysis of metal content in the final product

The samples were diluted with isopropanol and the content of Sr was determined in the obtained solutions using the HR-CS FAAS (High Resolution Continuum Source Flame Atomic Absorption Spectrometry) method (spectrometer contrAA 300 Analytik Jena, Germany).

3. Results and discussions

3.1. The specific surface area of binary oxides $(SrO)(Al_2O_3)$

The specified values of catalyst surface area (BET), monolayer capacity and average pore radius of mono- (γ-Al_2O_3) and bioxides ($(SrO)(Al_2O_3)$) are given in Table 1. The specific surface area measurements (BET) clearly showed that introduction of strontium ions into Al_2O_3 system caused decrease of specific surface area. Moreover the increase of calcination temperature to 900 or 1200 °C led to the same effect (Table 2).

The specific surface area goes down from 89 m²/g for binary oxide calcined at 600 °C to 77 and 2 m²/g for binary systems calcined at 900 and 1200 °C, respectively. These results are explained by the progressing process of phase crystallization and sintering process. The value of monolayer capacity decreases for catalytic systems together with increasing of calcination temperature. Whereas, completely different behaviour was seen in the case of the average pore radius. The lowest value of average pore radius had Al_2O_3 oxide in contradistinction to the binary system calcined at 900 °C, which exhibited the highest value equal 4.9 nm.
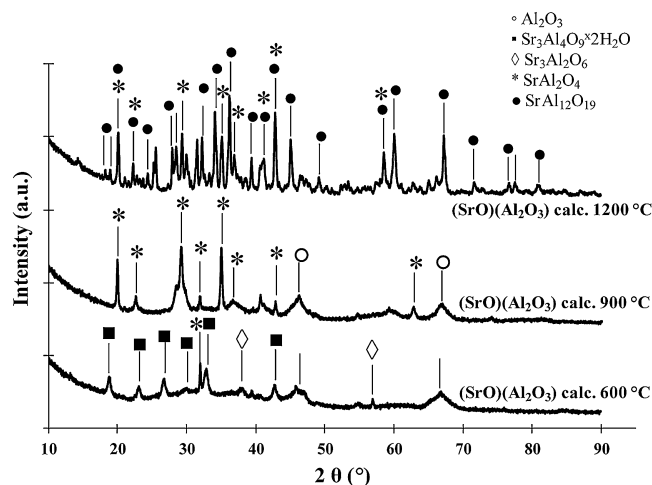
Fig. 1. XRD patterns for binary oxides after calcination for 4 h in air atmosphere at 600, 900 and 1200 °C.

3.2. The influence of calcination temperature on phase composition of $(SrO)(Al_2O_3)$ systems – XRD

The X-ray patterns of binary oxides after calcinations at 600, 900 and 1200 °C are shown in Fig. 1 and Table 3 (the quantitative phase analysis). The XRD data of the binary oxide $(SrO)(Al_2O_3)$ calcined at 600 °C confirmed the formation of $Sr_3Al_2O_6$, $Sr_3Al_4O_9\cdot2H_2O$ phases and spinel structure $SrAl_2O_4$ as a minor phase. Increasing of the calcination temperature to 900 °C causes crystallization of spinel phase (79 wt.% of $SrAl_2O_4$ see Table 3) and disappear reflexes originating from the other phases. In addition to the spinel phase only reflexes derived from the γ-Al_2O_3 phase (21 wt.%) were seen on the XRD curve recorded for $(SrO)(Al_2O_3)$ calcined at 900 °C. Further increase of the calcination temperature to 1200 °C caused decomposition of spinel structure and creation of new phase $SrAl_{12}O_{19}$ (see Fig. 1).

Baidya et al. [17] investigated the phase composition of Sr–Al mixed oxides prepared by co-precipitation method with a Sr/Al ratio from 0.25 to 1.5 and they detected the presence of several crystalline phases in the mixed oxides. XRD analysis of the mixed oxide confirmed the presence of multiple crystalline phases such as $SrAl_4O_7$, $SrAl_2O_4$, $Sr_3Al_2O_6$. Authors observed that the main phase was $Sr_3Al_2O_6$ which relative intensity increased with increasing Sr/Al ratio. Remaining reflexes observed for systems with low Sr loading gradually vanished with increasing Sr/Al ratio and fitted well to $Sr_3Al_4O_9\cdot2H_2O$ phase. It must be emphasized that their relative intensity was low compared to $Sr_3Al_2O_6$ phase. Authors reported that Sr–Al mixed oxides prepared by co-precipitation method were mixtures of $Sr_3Al_2O_6$ and $Sr_3Al_4O_9\cdot2H_2O$ crystalline phases, highlighting that $Sr_3Al_2O_6$ phase was the dominant phase.

Authors [17] studied also the phase composition of Sr–Al mixed oxide prepared by the reaction between various salts of Sr and Al_2O_3 and they observed that the formation of the crystalline phase strongly depended on the type of precursor. In the case of

Table 3
The quantitative analysis of $(SrO)(Al_2O_3)$ systems.

Sample	Calcination temperature (°C)	Phase composition	Quantitative phase analysis (wt.%)
$(SrO)(Al_2O_3)$	900	$SrAl_2O_4$	79
		γ-Al_2O_3	21
$(SrO)(Al_2O_3)$	1200	$SrAl_2O_4$	21
		$SrAl_{12}O_{19}$	51
		$Sr_4Al_{14}O_{25}$	28

application of the acetate precursor a mixture of $SrCO_3$ and $Sr_3Al_2O_6$ was formed. However, the use of the nitrate precursor leads to the formation of $Sr_3Al_2O_6$ phase. Whereas the use of hydroxide precursor in the reaction with aluminium oxide tended to form a mixture of $Sr_3Al_2O_6$ and $Sr_{12}Al_{14}O_{33}$ phases [18].

The phase composition of strontium aluminate precursor with CA/M = 2 (the molar ratio of citric acid to total metal cations concentration) and unadjusted pH after heating in air in the temperature range 700–1000 °C was also investigated by Qiu et al. [8]. The XRD curves recorded for system heating at 700 or 800 °C in air atmosphere for 2 h confirmed amorphous state of these systems. Increasing of the heating temperature to 900 °C results in the formation of single-phase $SrAl_2O_4$ spinel structure. These results are in line with our measurements. We also obtained spinel phase structure after calcination process carried out at 900 °C. Increasing the calcination temperature to 1000 °C caused increased crystallinity of the system.

While, the XRD analysis of the $SrAl_2O_4$ precursor with CA/M = 1 calcined in air atmosphere in temperature range 900–1300 °C for 2 h was also performed by Qiu et al. [8]. authors reported that calcination of $SrAl_2O_4$ precursor at 900 °C cause the formation of $SrAl_2O_4$, $SrAl_4O_7$ and $Sr_3Al_2O_6$ phases and pointed out that $SrAl_2O_4$ spinel structure is the major phase. Calcination of $SrAl_2O_4$ precursor at higher temperature 1100–1300 °C results in decreasing of the relative content of intermediate phases: $SrAl_4O_7$ and $Sr_3Al_2O_6$. On the diffraction curve recorded after calcination in air at 1300 °C only reflections coming from $SrAl_2O_4$ and $Sr_3Al_2O_6$ structure were evident, the diffraction peaks of $SrAl_4O_7$ disappeared. Based on their research, the authors concluded that the molar ratio between citric acid and total metal cations concentration has paramount importance for the formation temperature of $SrAl_2O_4$.

X-ray diffraction analysis of $SrAl_2O_4$ and $SrAl_{12}O_{19}$ prepared via ethylenediaminetetraacetic acid precursor route were performed by Xu et al. [10]. The XRD analysis performed for $SrAl_2O_4$ in the temperature range 700–1300 °C for 2 h showed that at 700 °C the analyzing powder is amorphous, increase of the calcination temperature to 800 °C caused crystallization of the monoclinic $SrAl_2O_4$ phase and the appearance of additional $SrAl_4O_7$ or $SrCO_3$ phase as intermediate phase. Further increase of the calcination temperature up to 1000 °C, caused the growth of $SrAl_2O_4$ phase crystallization, but the reflexes attributed to the intermediate phase were still visible. The diffraction peaks coming from additional phase disappears completely at 1200 °C and only single-phase $SrAl_2O_4$ spinel structure phase was detected on the XRD curve.

Similar XRD measurements were carried out for $SrAl_{12}O_{19}$ precursor in the temperature range 800–1400 °C. At 800 °C on the XRD curve two weak XRD-peaks at $2\theta = 46.0°$ and $67.1°$ were visible and assigned to the γ-Al_2O_3 phase. Calcination of $SrAl_{12}O_{19}$ precursor at 900 °C caused the appearance besides of γ-Al_2O_3 additional $SrAl_4O_7$ phase. Further raising the calcination temperature up to 1000 °C result in growth of $SrAl_4O_7$ phase crystallization. Starting from the 1200 °C the appearance of $SrAl_{12}O_{19}$ as a main phase and co-existence with $SrAl_4O_7$ as a intermediate phase were detected. Calcination of the starting material at 1300° C leads to the formation of the main phase $SrAl_{12}O_{19}$ together with a trace of $SrAl_4O_7$ phase, while after calcination at 1400 °C the only structure observed on the diffraction curve was pure $SrAl_{12}O_{19}$ phase.

3.3. The impact of the activation temperature on the basic properties of binary oxides

Temperature-programmed desorption of carbon dioxide is a conventional method for characterizing alkalinity of heterogeneous catalysts. Carbon dioxide desorption profiles of $(SrO)(Al_2O_3)$ systems calcined at 600, 900 and 1200 °C are given in Fig. 2. The

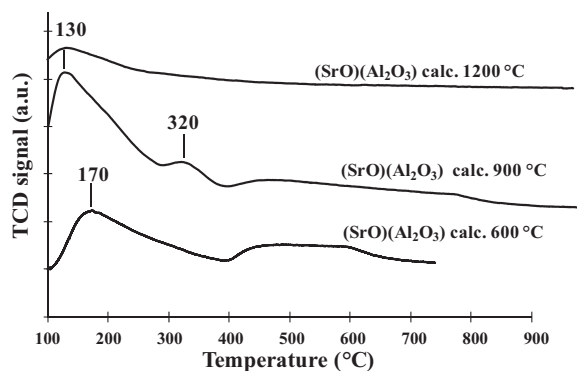**Fig. 2.** TPD-CO_2 profile recorded for $(SrO)(Al_2O_3)$ binary systems calcined for 4 h in air atmosphere at 600, 900 and 1200 °C.

quantitative analysis (the amount of CO_2 adsorbed on $(SrO)(Al_2O_3)$ systems) is collected in Table 4.

TPD-CO_2 profiles exhibited three desorption stages for all investigated materials. This suggests that in $(SrO)(Al_2O_3)$ systems there are basic centres with different strength (weak, medium and strong). The results gave evidence that system which was previously calcined at 900 °C desorbs the greatest amount of CO_2 in the temperature range 100–600 °C compared to other studied materials what means that $(SrO)(Al_2O_3)$ binary oxide calcined at 900 °C is the most basic catalyst system. This observation was evidenced by quantitative analysis. The quantitative analysis showed that the amount of adsorbed CO_2 on the surface of $(SrO)(Al_2O_3)$ system calcined at 900 °C is the highest and it is 0.1022 mmol g^{-1}. It is two times higher than for sample calcined at 600 °C (0.0538 mmol g^{-1}) and four times higher than for $(SrO)(Al_2O_3)$ calcined at 1200 °C (0.0025 mmol g^{-1}). This basicity properties have important influence on catalytic activity of $(SrO)(Al_2O_3)$ catalysts in transesterification reaction.

3.4. Surface sorption properties of binary systems

In order to clarify and understanding of the differences in catalytic activity of binary oxide systems using in transesterification reaction the surface adsorbed species formed during methanol adsorption on catalyst surface were investigated by FTIR technique. Fig. 3 demonstrates the IR spectra collected after the exposure of investigated binary systems to a 1 vol.% CH_3OH in argon stream under atmospheric pressure at 50 °C. The IR spectra gathered for $(SrO)(Al_2O_3)$ systems calcined at 600, 900 and 1200 °C showed several characteristic bands. The visible bands located at 2943, 2897, 2823, 1720, 1448 and 1370 cm^{-1} were observed for all investigated systems and were attributed to the HCOO–Sr species.

In addition to the formate surface species carbonate species were also detected (CO_3^{2-}–Sr) visible respectively at the following wavelengths: 1685, 1570–1440, and 1236 cm^{-1}. Apart from those mentioned surface species formed after methanol exposure strontium methoxide CH_3O–Sr situated at 1060, 1120, 1200, 1236, 1371, 1448 cm^{-1} and aluminium methoxide CH_3O–Al: positioned in the wavelength range 1020–1100 cm^{-1} species have also been

Table 4
The amount of CO_2 adsorbed on $(SrO)(Al_2O_3)$ samples calcined in different temperature measured from TPD-CO_2 data.

Sample	Calcination temperature (°C)	The amount of adsorbed CO_2 (mmol g^{-1})
$(SrO)(Al_2O_3)$	600	0.0538
$(SrO)(Al_2O_3)$	900	0.1022
$(SrO)(Al_2O_3)$	1200	0.0025
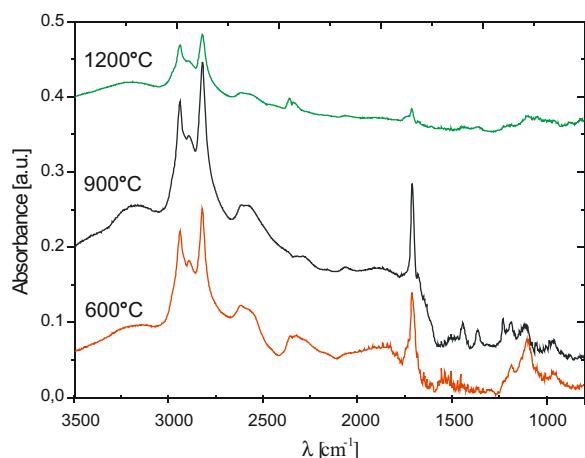
Fig. 3. Infrared spectra of adsorbed species taken after heating at 400 °C in the Ar mixture and exposure of the following catalytic systems: $(SrO)(Al_2O_3)$ calcined in air at 600 °C for 4 h, $(SrO)(Al_2O_3)$ calcined in air at 900 °C for 4 h, and $(SrO)(Al_2O_3)$ calcined in air at 1200 °C for 4 h to a 1 vol.% methanol–argon mixture at 50 °C.

observed. Moreover, on the IR spectrum the appropriate bands seen at 2180 cm^{-1} attributed to gaseous CO and gaseous CO_2 assigned to the bands positioned at 2360 and 2320 cm^{-1} were also detected after methanol adsorption. From the IR measurements we can easily conclude that the greatest quantity of adsorbed methanol was observed for binary system calcined at 900 °C which is a mixture of $SrAl_2O_4$ spinel structure and γ-Al_2O_3 phases. In the case of this system the higher quantity of metoxide is formed over the surface what is very important stage of the transesterification reaction and plays an crucial role in the considered process.

3.5. The effect of calcination temperature on the structure of $(SrO)(Al_2O_3)$ binary oxides

A scanning electron microscope (SEM) S-4700 (HITACHI, Japan), equipped with an energy dispersive spectrometer EDS (Thermo Noran, USA) was employed to characterize the morphology and determination of elemental distribution of $(SrO)(Al_2O_3)$ binary systems. The results of SEM-EDS measurements for $(SrO)(Al_2O_3)$ after at 900 and 1200 °C are given in Figs. 4a and b, respectively.

The magnification was equal 5000 in all cases. The distribution of strontium, aluminium and oxygen for investigated binary oxide are also shown in the same figure. The EDS images collected from the surface showed that the distribution of Sr, Al and O is inhomogeneous for all samples. The distributions of each element for $(SrO)(Al_2O_3)$ binary oxides calcined at 900 °C showed that strontium, aluminium and oxide are visible in the same location on the surface. This result suggests that the spinel structure is formed in the case of $(SrO)(Al_2O_3)$ calcined at 900 °C. Whereas, $(SrO)(Al_2O_3)$ calcined at 600 or 1200 °C were the mixtures of $SrAl_2O_4$ and other Sr–Al oxides phase which were detected by XRD technique.

3.6. The influence of the catalyst pre-treatment and reaction condition on the activity results

In the first step of analysis of the reaction products we conducted the quantitative analysis of derivatized rapeseed oil (a process of derivatization of raw material to fatty methyl esters was done according to the international standard ISO 12966-2:2011). The composition of rapeseed oil after the process of derivatization was analyzed by GC–MS method and the results are shown in Table 5.

The quantitative studies performed for derivatized rapeseed oil showed that the main components of the oil are esters of following fatty acid: palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic

Table 5
The chemical composition of the rapeseed oil after the process of derivatization.

Fatty acid components	Values (%)
C16:0	2.7
C18:0	4.4
C18:1	60.1
C18:2	21.8
C22:0	3.6
C22:1	4.0
Others	3.4

(C18:2), bohenic (C22:0) and erucic (C22:1). The obtained results agree well with the quantitative and qualitative analysis relating to rapeseed oil composition.

The efficiency of transesterification reaction and quality of obtained biodiesel depends strongly on the conditions applied in the process. Absolutely important is to optimize the reaction conditions carried out for improve the reaction yield. The most known factors which have decisive influence on the reaction are: reaction time, type of catalyst and its quantity, temperature of the reaction, the molar ratio between oil and methanol and catalyst activation conditions [2].

In this work, the following parameters including: reaction time, reaction temperature, molar ratio between oil and methanol, catalyst pre-treatment and catalyst concentration which have a direct impact on the investigative process were studied.

The HPLC chromatograms of triglycerides belonging to the rapeseed oil, methyl esters of fatty acids formed on the derivatization step of rapeseed oil and the final transesterification reaction product obtained over $SrAl_2O_4$ catalyst calcined at 600 °C (reaction conditions: reaction temperature $T = 160$ °C, mass of the catalyst $m = 1.95$ g, reaction time $t = 2$ h, molar ratio Oil: methanol = 1: 6), are shown on Fig. 5.

Table 6 shows the activity results of the $(SrO)(Al_2O_3)$ bioxide system using in transesterification process at various reaction temperature, for different molar ratio between rapeseed oil and methanol and for various catalysts loading. The influence of the catalyst content and various temperature activation (calcination temperature) on the TG conversion and FAME yield was also studied in this work and the obtained results are given in the same Table 6. The catalytic activity results carried out for catalytic systems in studied reaction show that increasing of catalyst quantity and calcination temperature leads to an enhanced of triglycerides (TG) conversion and FAME yield. The optimum activation temperature was calcination of $(SrO)(Al_2O_3)$ binary oxide in air atmosphere for 4 h at 900 °C. Catalytic system which was calcined at this temperature exhibited higher TG conversion equal 86% in the same reaction conditions in comparison to system activated at 600 and 1200 °C (weight of catalyst = 1.95 g, molar ratio oil: methanol = 1: 6, reaction time 1 h, reaction temperature 160 °C). Further increasing of calcination temperature to 1200 °C did not cause improvement of activity. These results clearly confirm the promotion effect of spinel like structure on catalytic activity in transesterification reaction. The XRD measurement conducted for $(SrO)(Al_2O_3)$ binary oxide calcined at 900 °C showed the presence of the main phase $SrAl_2O_4$ spinel structure and the remaining phase γ-A_2O_3. The formation of stable spinel structure limits the passage of strontium ions to the reaction solution as in the case for the same system calcined at 600 °C. On the other hand the decrease of TG conversion in transesterification reaction of rapeseed oil carried out over $(SrO)(Al_2O_3)$ system calcined at 1200 °C may be elucidate by the lowest surface area, lower sorption capacity of methanol and by the structure of this system (see XRD measurements).

The analysis of the strontium content in the reaction product were also studied in this work and the influence of several factors like reaction time, catalyst loading molar ratio oil: methanol
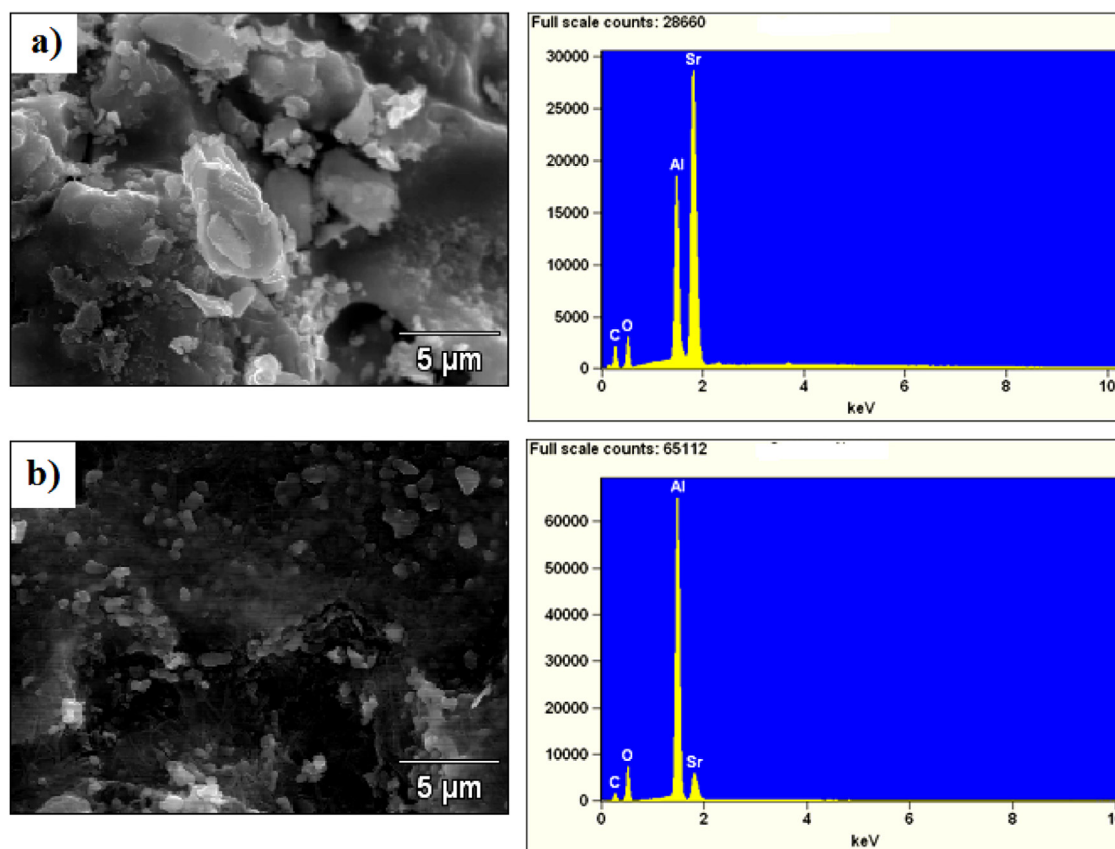
Fig. 4. SEM images of $(SrO)(Al_2O_3)$ calcined at $900\,^{\circ}C$ (a) and at $1200\,^{\circ}C$ (b).

were investigated. The results obtained using High Resolution Continuum Source Flame Atomic Absorption Spectrometry were presented in Table 6. The metal content analysis showed that the crystallization process caused the decrease of the strontium concentration in the final solution, the same effect was observed for the reaction operated at a higher molar ratio between oil: methanol and conducted over a longer period of time (2 and 4 h).

Summing up the results of activity in correlation with the characteristics of the tested catalysts must be held that the high activity of $(SrO)(Al_2O_3)$ system calcined at $900\,^{\circ}C$ should be associated with the greatest basicity and high sorption capacity with respect to methanol at $50\,^{\circ}C$ what was confirmed by FTIR technique. Furthermore, the presence of the spinel structure $SrAl_2O_4$ in its composition play crucial role in transesterification reaction. Spinel structure stability strongly limits the passage of strontium ions into the final reaction product. Sr^{2+} ion are the active centres in this reaction, on these centres mainly occurs the methanol adsorption as the one of the reactants of the studied reaction and

Table 6
Effect of catalyst/oil molar ratio, reaction temperature, reaction time, catalyst activation on the catalytic performance of $(SrO)(Al_2O_3)$ catalyst in transesterification of rapeseed oil process and the strontium content in the final product.

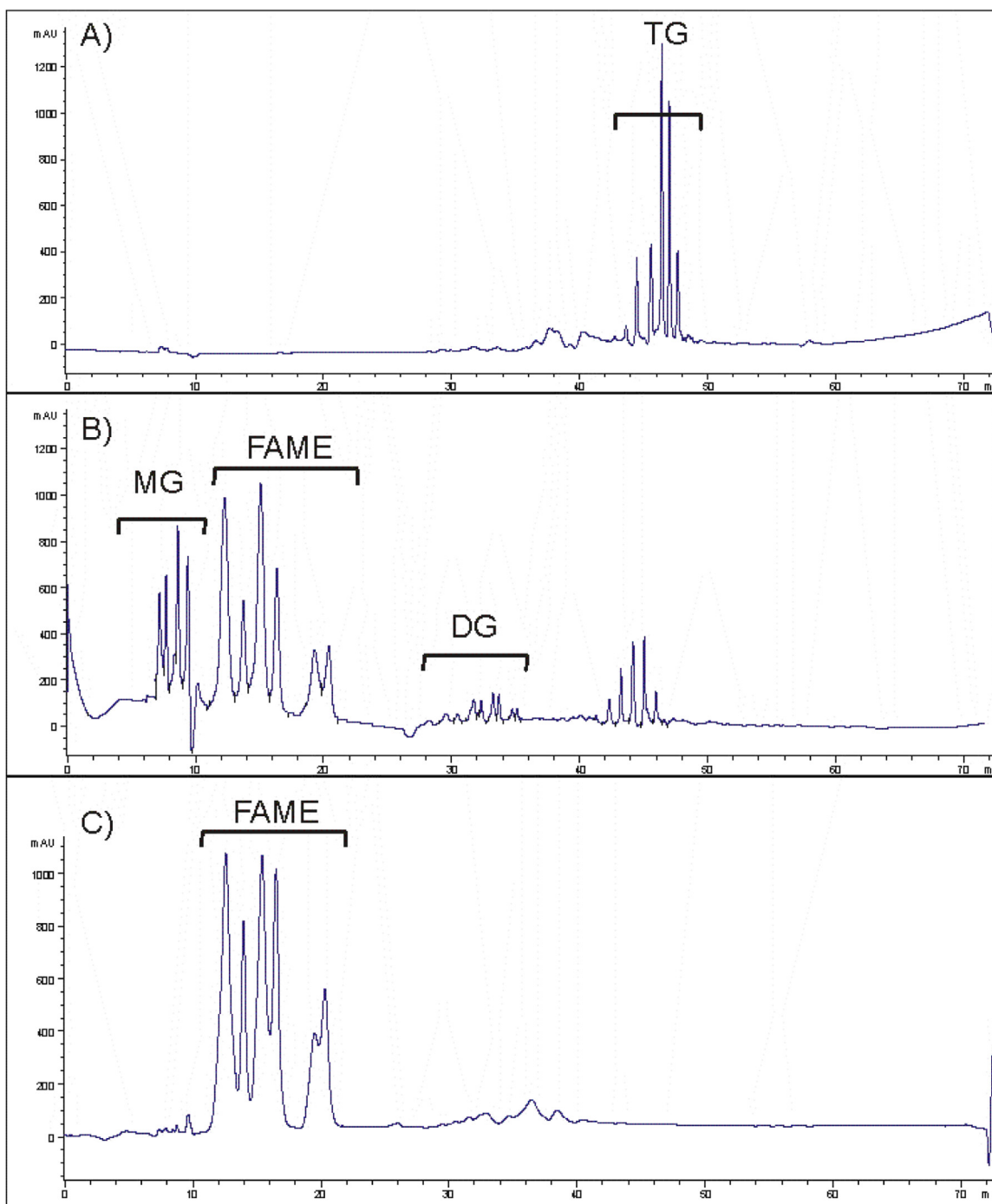| Catalyst	Reaction temperature (°C)	Reaction time (h)	Molar ratio oil: methanol	Calcination temperature (°C)	Catalyst weight (g)	Triglycerides conversion (%)	Strontium content in the final product (mg/L)	FAME yield (%)
The effect of reaction temperature for catalytic activity of (SrO)(Al$_2$O$_3$) in transesterification								
SrAl$_2$O$_4$	100	1	1 : 6	600	1.95	33	–	–
SrAl$_2$O$_4$	140	1	1 : 6	600	1.95	56	–	–
SrAl$_2$O$_4$	160	1	1 : 6	600	1.95	*62*	–	–
The effect of mass of catalysts for catalytic activity of (SrO)(Al$_2$O$_3$) in transesterification								
SrAl$_2$O$_4$	160	1	1 : 6	600	1.0	40.5	31.3	19
The effect of CH$_3$OH:oil ratio for catalytic activity of (SrO)(Al$_2$O$_3$) in transesterification								
SrAl$_2$O$_4$	160	1	1 : 9	600	1.95	80.5	77.3	77
SrAl$_2$O$_4$	160	1	1 : 12	600	1.95	20.2	51.4	4
The effect of reaction time for catalytic activity of (SrO)(Al$_2$O$_3$) in transesterification								
SrAl$_2$O$_4$	160	4	1 : 6	600	1.95	88.3	286	90
SrAl$_2$O$_4$	160	2	1 : 6	*600*	1.95	*90.5*	*319*	*89*
The effect of calcination temperature for catalytic activity of (SrO)(Al$_2$O$_3$) in transesterification								
SrAl$_2$O$_4$	160	1	1 : 6	*900*	1.95	*86*	*7.62*	*85*
SrAl$_2$O$_4$	160	1	1 : 6	*1200*	1.95	*74*	*0.62*	–

Fig. 5. HPLC chromatogram of (A) rapeseed oil (B) final transesterification reaction product and (C) fatty acid methyl ester (FAME).

then adsorbed methanol can further transform to the methoxide species. In this case the transesterification reaction is then controlled by the mass-transfer. Our results agree well with the earlier report that the rate of transesterification reaction strongly depend on the rate of methoxide species formation and the efficiency of the solid catalyst is related of their formation [19].

The confirmation of the stability of $(SrO)(Al_2O_3)$ system calcined at 900 °C was the analysis of the metal content (strontium content) in the final product. The $(SrO)(Al_2O_3)$ binary oxide calcined at 900 °C is separated easily from the reaction mixture and the formation of the spinel phase after activation process carried out at 900 °C in air atmosphere for 4 h restricts the strontium quantity passing to the reaction product (see Table 6). The observed a small amount

of strontium in the reaction product produced in transesterification reaction over binary oxide calcined at 900 °C comes from the amount of Sr^{2+} which has not formed a spinel $SrAl_2O_4$ structure.

4. Conclusion

In summary, we have demonstrated that binary oxides $(SrO)(Al_2O_3)$ catalysts activity in transesterification of rapeseed oil depends on their structure and the reaction conditions. We found that the composition of binary oxides is a function of activation temperature. TG conversion and FAME yield is strongly associated with the activation temperature, reaction conditions (time and temperature of studied reaction, molar ratio between substrates,

catalyst loading). It was proven that the highest TG conversion and FAME yield was obtained over $(SrO)(Al_2O_3)$ system calcined at 900 °C. It appears that a high activity is explained by the structure of this system. The presence of the spinel structure $SrAl_2O_4$ (79 wt.%) as the major phase of $(SrO)(Al_2O_3)$ system calcined at 900 °C limits the passage of strontium ions into the reaction solution and causing also an increase in the sorption properties of methanol and also increases the total basicity.

Acknowledgment

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